A Unique Approach to the Synthesis of 2,3,4,5-Substituted Polybrominated Biphenyls: Quantitation in FireMaster FF-1 and FireMaster BP-6

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A scheme is presented that allows the efficient synthesis of four anilines (3,5-di-, 3,4,5-tri-, 2,3,4,5-tetra-, and 2,3,4,5,6-pentabromoanilines) as well as 1,2,3,4-tetrabromobenzene from a single starting material. All of these products are useful precursors in the synthesis of polybrominated biphenyls (PBBs). The aryl–aryl coupling of bromoanilines with 1,2,3,4-tetrabromobenzene provides a versatile approach to the synthesis of 2,3,4,5-tetrasubstituted PBBs for the first time. The synthesis and characterization of nine such PBBs are reported here. Interestingly, aside from the desired coupling product, the 2,2′,3,3′,4,4′,5,5′-octabromobiphenyl was a byproduct of each coupling reaction, ranging from less than 2% to 63% of the polybrominated biphenyl products. Capillary gas chromatographic quantitation of the nine synthetic PBBs in fireMaster FF-1 and fireMaster BP-6 is presented.

Mixtures of polybrominated biphenyls (PBBs) were synthesized commercially as fire-retardant chemicals and were sold under the trade name fireMaster. These products were of minor commercial importance but gained national attention after an accident that occurred in 1973, in which the commercial PBB mixture fireMaster FF-1 was unintentionally substituted for nutriMaster, a magnesium oxide cattle feed supplement. The direct addition of fireMaster into feeds resulted in a major pollution disaster primarily confined to the state of Michigan (Robertson and Chynoweth, 1975; Kay, 1977). The initial high-level contamination of feed and livestock (Jackson and Halbert, 1974) ultimately resulted in the widespread contamination of the food chain (DiCarlo et al., 1978), and PBB residues were detected in wildlife and in the general population of Michigan. Because of their lipophilic character, PBBs, like other halogenated compounds such as polychlorinated biphenyls (PCBs), are stored in adipose tissue and have been identified in human blood, fat, and breast milk (Eyster et al., 1983).

PBBs are not unlike other toxic halogenated aromatic hydrocarbons, including 2,3,7,8-tetrachlorodibenzo-*p*-dioxin (Poland and Knutson, 1982; Poland and Glover, 1980), in causing weight loss, thymic atrophy, liver damage, endocrine disorders, and various skin lesions in laboratory animals (Gupta and Moore, 1979; Gupta et al., 1981, 1983a,b). In addition, PBBs are potent inducers of a variety of drug-metabolizing enzymes, including several forms of cytochrome P-450 (Dent et al., 1976; Parkinson et al., 1983; Dannan et al., 1983; Robertson et al., 1982, 1984). The toxicity and persistence of PBBs dictate that the analytic or synthetic chemist use extreme care while handling these compounds.

The human health impact of PBBs has not been delineated. A major obstacle to studying these compounds has been the unavailability of analytic standards and pure individual isomers and congeners for animal studies. This paper describes a new approach to the synthesis of 2,3,4,5-substituted PBBs and their identification by high-resolution capillary GC and GC–MS of several new PBB components in fireMaster FF-1 and fireMaster BP-6.

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EXPERIMENTAL SECTION

4-Bromoaniline, 2,4- and 2,5-dibromoaniline, and **2,6-dibromo-4-nitroaniline (I)** were purchased from Aldrich Chemical Co., Milwaukee, WI, while 3,4-dibromoaniline and amyl nitrate were purchased from Pfaltz & Bauer, Stamford, CT. FireMaster BP-6, Lot 7062, was provided by the Michigan Chemical Co., St. Louis, MI, and fireMaster FF-1, Lot FH 7042, was obtained from FDA.

2,4,5-Tribromoaniline was prepared from 2,5-dibromoaniline as previously described (Robertson et al., 1980) with the improvement that bromination using NBS was carried out in acetonitrile at 60 °C (Nickson and Roche-Dolson, 1985; Mitchell et al., 1979). Halogenation occurred exclusively in the 4-position. The compound was purified as described for VIII: mp 81 °C (methanol/water); yield 85%; purity >99% by GC.

3,5-Dibromonitrobenzene (II) was prepared from I by a reductive deamination in hypophosphorus acid (Kornblum, 1944). A 60-g portion (0.21 mol) of I was suspended in 500 mL of 50% sulfuric acid and diazotized with a 10% aqueous sodium nitrite solution (13.8 g of sodium nitrite (0.2 mol) in 140 mL of water) at 0 °C. The suspension was stirred for several hours and allowed to warm to room temperature. Hypophosphorus acid (50%, 144 mL) was added to the almost-clear solution, dropwise, and the reaction was stirred overnight. The product was filtered and purified by continuous extraction over alumina with *n*-hexane and recrystallized: mp 104 °C (*n*-hexane; 105–105.5 °C; Qvist and Grönroos, 1960); yield 72%; purity >99% by GC. Structure was confirmed by MS, molecular ion at m/e 281, and ^{1}H NMR in deuterated methylene chloride: 8.02 (t, J = 1.69 Hz, H4), 8.32 ppm (d, J = 1.71 Hz, H2, H6).

3,5-Dibromoacetanilide (III). A 60-g portion (0.20 mol) of II was dissolved in 400 mL of glacial acetic acid–acetic anhydride (3:1, v/v). Finely divided iron (Merck, Darmstadt, FRG) was added stepwise at room temperature, and the reaction was monitored by silica gel TLC (methanol–chloroform, 1:9, v/v). The crude product was poured onto ice, filtered, dried, extracted in boiling methanol, and recrystallized: mp 227–228 °C (methanol) with slight decomposition; yield 97%; purity >99% by GC. The structure was verified by MS, molecular ion at m/e 293, and ^{1}H NMR in deuterated methylene chloride: 2.12 (s, CH_3), 7.21 (s, NH), 7.38 (t, J = 1.7 Hz, H4), 7.66 ppm (d, J = 1.7 Hz, H2, H6).

3,5-Dibromoaniline (IV) was prepared from 60 g (0.24 mol) of III by stirring this compound in 400 mL of ethanol–HCl suspension (1:1, v/v) at 80–90 °C for 2 h. The crude reaction mixture was then poured onto ice, washed with sodium hydroxide until neutral, and recrystallized: mp 54–55 °C (methanol–water, 5:9, v/v; 54 °C; Hayashi, 1956); yield 90%; purity > 97% by GC. The

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structure was confirmed by MS, molecular ion at m/e 251, and ^{1}H NMR in deuterated methylene chloride: 3.84 (s, NH_2), 6.74 (d, J = 1.61 Hz, H2, H6), 6.97 ppm (t, J = 1.58 Hz, H4).

3,4,5-Tribromonitrobenzene (V) was prepared from I by a Sandmeyer reaction with sodium nitrate and cuprous bromide–hydrobromic acid. A 50-g portion (0.16 mol) of I was suspended in 400 mL of cooled 50% sulfuric acid with stirring and the solution allowed to warm to room temperature. A 10% aqueous solution of sodium nitrite (13 g of sodium nitrite (0.19 mol) in 130 mL of water) was added dropwise, and the suspension was stirred for 2 h, at which time urea was added. The almost-clear solution was poured onto cuprous bromide–hydrobromic acid (50 g of CuBr in 200 mL of hydrobromic acid) and stirred for additional 30 min. The product was filtered, washed with water, dried, and purified by alumina chromatography using n-hexane: mp 112 °C (n-hexane; 112 °C; Hayashi, 1956); yield 91%; purity >99% by GC. The structure was confirmed by MS, molecular ion at m/e 357, and ^{1}H NMR in deuterated methylene chloride: 8.45 ppm (s, H2, H6).

3,4,5-Tribromoacetanilide (VI) was prepared by the reaction of V with acetic anhydride and iron. A 60-g portion (0.17 mol) of V was suspended in 400 mL of glacial acetic acid–acetic anhydride (3:1, v/v), and the reaction mixture was heated to 80 °C. Finely divided iron (Merck) was added, and the reaction was monitored by silica gel TLC (methanol–chloroform, 1:9, v/v). The crude reaction mixture was poured onto ice, from which the product was filtered, washed, and dried: mp 260 °C (methanol–water; 241–242 °C; Furuyama and Fukushi, 1971); yield 97%; purity >98% by GC. Structure was confirmed by MS, molecular ion at m/e 369, and ^{1}H NMR in deuterated methylene chloride: 2.12 (s, CH_3), 2.14 (s, CH_3), 7.23 (s, NH), 7.85 ppm (s, H2, H6).

3,4,5-Tribromoaniline (VII) was prepared by the deacetylation of VI. A 60-g portion (0.16 mol) of VI was suspended in 400 mL of ethanol–hydrochloric acid (1:1, v/v) and with vigorous stirring was warmed to 80–90 °C. The reaction was monitored by silica gel TLC (methanol–chloroform, 1:9, v/v). The crude product was poured onto ice, filtered, and resuspended in water, and 1 N aqueous sodium hydroxide was added until the suspension remained basic: mp 130 °C (methanol–water; 129–130 °C; Furuyama and Fukushi, 1971); yield 96%; purity >98% by GC. The structure was verified by MS, molecular ion at m/e 327, and ^{1}H NMR in deuterated methylene chloride: 3.89 (s, NH_2), 6.94 ppm (s, H2, H6).

2,3,4,5-Tetrabromoaniline (VIII) was prepared by the bromination of VII. A 120-g portion (0.36 mol) of VII was dissolved in 800 mL of acetonitrile, the resultant mixture warmed to 60 °C, and a solution of NBS in acetonitrile added until the reaction was complete as monitored by GC. The crude reaction mixture was filtered, and the filtrate was evaporated to dryness. The product was obtained by recrystallization: mp 138 °C (methanol–water; 130–137 °C; Furuyama and Fukushi, 1971); yield 86%; purity >99% by GC. The structure was confirmed by MS, molecular ion at m/e 409, and ^{1}H NMR in deuterated methylene chloride: 4.45 (s, NH_2), 7.11 ppm (s, H6).

2,3,4,5,6-Pentabromoaniline (IX) was prepared by the addition of 8.2 g (0.14 mol) of bromine to 6 g (0.14 mol) of VIII in 240 mL of chloroform at room temperature. The crude reaction mixture was filtered, and the filtrate was evaporated to dryness. The product was obtained by recrystallization: mp 265 °C (methanol–water; 260 °C; Hantzsch and Smythe, 1900); yield 91%; purity > 99% by GC. The structure was confirmed by MS, molecular ion at m/e 483, and ^{1}H NMR in deuterated methylene chloride: 5.1 ppm (s, NH_2). An incomplete description of the synthesis and characterization of compounds V and VII–IX has been previously reported (Robertson et al., 1981).

1,2,3,4-Tetrabromobenzene (X) was prepared by deamination of VIII. A 60-g portion (0.14 mol) of VIII was suspended in 500 mL of cooled 50% sulfuric acid, and with rapid stirring a 10% aqueous solution of sodium nitrite (13.8 g of sodium nitrite (0.2 mol) in 140 mL of water) was added dropwise. The resulting solution was stirred for an additional 2 h at which time 144 mL of 50% hypophosphorous acid was added slowly, and the reaction was stirred overnight. The reaction mixture was poured onto ice, filtered, and dried. The product was purified by alumina chromatography with n-hexane and recrystallized: mp 60–61 °C (n-hexane; 58–59 °C; Furuyama and Fukushi, 1971); yield 90%; purity >99% by GC. The structure was confirmed by MS, molecular ion at m/e 394, and ^{1}H NMR in deuterated methylene chloride: 7.49 ppm (s, H5, H6).

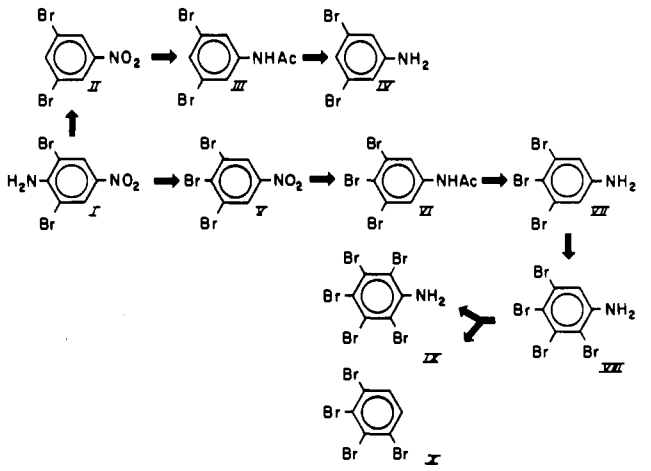

Figure 1. Synthetic scheme for polybrominated biphenyl precursors.

PBBs were prepared by the diazo coupling of the corresponding brominated anilines with excess of 1,2,3,4-tetrabromobenzene (which also served as the solvent medium) as previously described (Robertson et al., 1984). The products were purified by alumina/Florisil column chromatography, followed by repeated recrystallization from methanol or methylene chloride and flash chromatography. The structures of all PBBs were confirmed by 400-MHz ^{1}H NMR spectrometry (Bruker AM-400, in deuterated methylene chloride) and by MS (Varian Ch-7a operated in the EI mode at 70 eV, sample introduction by direct insertion). ^{1}H NMR and mass spectra were recorded at the Institute of Organic Chemistry, University of Mainz, FRG. Absorption spectroscopy was carried out on a Shimadzu MPS-2000 spectrophotometer, equipped with a Shimadzu PR-3 graphic printer.

GC determinations of product purity were performed on a Packard 427 gas chromatograph, equipped with a Packard 603 integrator and a 2 mm (i.d.) × 2 m column of 3% OV 17 (50% phenylmethylsilicone) on Chromosorb WAW-DMCS (80–100 mesh). The temperature program was 150–320 °C (8 °C/min; hold at final temperature). The temperature of the injector was 300 °C, and that of the detector, 340 °C.

Measurement of relative retention times and relative response factors of the authentic PBB standards were carried out at the University of Reading, England, on a Pye-Unicam 204 gas chromatograph equipped with a ^{63}Ni electron capture detector and a HP 3090 A integrator fitted with a Grob/splitless injector. The column was a bonded-phase 25-m vitreous silica capillary column BP-5 (5% phenylmethylsilicone), i.d. 0.33 mm and o.d. 0.42 mm. The injector head pressure was 4 psi, and the carrier gas flow was kept constant at 1 mL/min (31.7 cm/s). The temperature program was 50 °C for 2 min and then 20 °C/min to 220 °C. The injector temperature was 230 °C, and that of the detector was 250 °C.

GC-MS quantitation and confirmation of the fireMaster components were carried out on a Carlo-Erba 5060 gas chromatograph interfaced with a VG 7070 F double-focusing mass spectrometer (EI, 70 eV). GC column and conditions were identical with those described for the GC-ECD retention time determinations above. Quantitation was based on ion collection of the respective molecular ions in the EI mode.

RESULTS AND DISCUSSION

The synthetic methods and purification of PBB precursors described in this paper allowed products to be obtained in good yields and in higher purity than was previously possible (Robertson et al., 1981, 1982). The highly efficient synthetic plan (Figure 1) permitted the use of almost every product, with the exception of the acetanilides, as a precursor in the synthesis of the desired PBBs. The reduction of the nitro compounds to the acetanilides, although requiring an additional synthetic

Table I. Synthesis and Characterization of the PBBs

no.[a]	synthetic PBB (yield,[b] %)	precursors	mp, °C	UV: λ_{max},[c] nm
114	2,3,4,4′,5-pentabromobiphenyl (2.8)	4-bromoaniline, 1,2,3,4-tetrabromobenzene	128	222.6 (54.8) [258][d]
137	2,2′,3,4,4′,5-hexabromobiphenyl (2.3)	2,4-dibromoaniline, 1,2,3,4-tetrabromobenzene	124	223.1 (35.4)
141	2,2′,3,4,5,5′-hexabromobiphenyl (1.5)	2,5-dibromoaniline, 1,2,3,4-tetrabromobenzene	127	223.4 (191)
156	2,3,3′,4,4′,5-hexabromobiphenyl (1.1)	3,4-dibromoaniline, 1,2,3,4-tetrabromobenzene	178	224.9 (229) [259][d]
159	2,3,3′,4,5,5′-hexabromobiphenyl (2.5)	3,5-dibromoaniline, 1,2,3,4-tetrabromobenzene	195	226.1 (61.4) [258][d]
180	2,2′,3,4,4′,5,5′-heptabromobiphenyl (3.2)	2,4,5-tribromoaniline, 1,2,3,4-tetrabromobenzene	166	224.1 (62.4)
189	2,3,3′,4,4′,5,5′-heptabromobiphenyl (6.4)	3,4,5-tribromoaniline, 1,2,3,4-tetrabromobenzene	219	230.7 (102) [265][d]
194	2,2′,3,3′,4,4′,5,5′-octabromobiphenyl (7.1)	2,3,4,5-tetrabromoaniline, 1,2,3,4-tetrabromobenzene	235	223.7 (51.6)
206	2,2′,3,3′,4,4′,5,5′,6-nonabromobiphenyl (1.1)	2,3,4,5,6-pentabromoaniline, 1,2,3,4-tetrabromobenzene	262	225.2 (131)

[a] Adopted from Ballschmitter and Zell, 1980. [b] Percent of theoretical yield of the coupling reaction. [c] In *n*-heptane; ϵ in parentheses; k-band maxima, if present, in brackets. [d] Shoulder.

step, was a more efficient (and a cleaner) reaction than was the direct reduction of the nitro compounds by other methods.

In contrast to the synthesis of the precursors, the Cadogan variation of the Gomberg–Bachmann coupling reaction (Gomberg and Bachmann, 1924; Cadogan, 1962), the last synthetic step in PBB synthesis, is a low-yield synthetic reaction (Table I). The inefficiency of this reaction is explained only in part by the formation of several byproducts, including polybrominated azobenzenes and terphenyls. In addition, steric hindrance does not appear to play a major role since the yield in the synthesis of several higher halogenated biphenyls, e.g. 2,3,3′,4,4′,5,5′-heptabromobiphenyl (189), was higher than that of several less halogenated congeners, e.g. 2,3,4,4′,5-pentabromobiphenyl (114). Also affecting yield was the formation of the 2,2′,3,3′,4,4′,5,5′-octabromobiphenyl (194), a compound detected in each PBB preparation, ranging from less than 2% to 63% of the PBB products. The mechanism by which 2,2′,3,3′,4,4′,5,5′-octabromobiphenyl (194) could have been formed in each coupling reaction, regardless of the aniline starting material, is unclear. The radical nature of the Gomberg–Bachmann reaction is well supported (Beadle et al., 1984; Gragerov et al., 1968; Rüchardt et al., 1964; Vernin et al., 1974). A possible explanation for the formation of the 2,2′,3,3′,4,4′,5,5′-octabromobiphenyl (194) could involve the intermediacy of a free radical, namely the 2,3,4,5-tetrabromophenyl radical, which is stabilized by σ-delocalization of the *o*-bromo substituent. The coupling reactions of corresponding chloro-substituted compounds do not produce these undesired symmetrical coupling products (unpublished observation). The radical transfer in these cases is less favored since the σ and σ^* C–Cl bonds do not allow a comparably effective σ-delocalization of the unpaired electron. As far as we know, radical transfer reactions of this type representing an additional proof of the radical nature of Gomberg–Bachmann reaction have not been reported.

All ^{1}H NMR spectra were fully consistent with the proposed structures (Table II). In accordance with the findings of Mullin and co-workers for polychlorinated biphenyls (Mullin et al., 1981, 1984), the protons of the synthetic PBBs were deshielded in the order ortho (7.09–7.61 ppm), meta (7.56–7.97 ppm), and para (7.45, 7.76 ppm). Only in the case of compound 141 was the resonance of the meta proton (7.56 ppm) of lower field than that of the para proton.

Table II. 400-MHz Proton Magnetic Resonance Data of the Synthetic PBBs in Deuterated Methylene Chloride

no.[a]	synthetic PBB	δ (J, Hz)
114	2,3,4,4′,5-pentabromobiphenyl	7.58 (H6, s) 7.22 (H2′, H6′, m) 7.59 (H3′, H5′, m)
137	2,2′,3,4,4′,5-hexabromobiphenyl	7.52 (H6, s) 7.87 (H3′, d, J = 1.91) 7.56 (H5′, dd, J = 8.21/1.95) 7.09 (H6′, d, J = 8.19)
141	2,2′,3,4,5,5′-hexabromobiphenyl	7.52 (H6, s) 7.56 (H3′, d, J = 8.55) 7.45 (H4′, dd, J = 8.55/2.38) 7.36 (H6′, d, J = 2.37)
156	2,3,3′,4,4′,5-hexabromobiphenyl	7.58 (H6, s) 7.61 (H2′, d, J = 2.09) 7.71 (H5′, d, J = 8.25) 7.17 (H6′, dd, J = 8.25/2.13)
159	2,3,3′,4,5,5′-hexabromobiphenyl	7.57 (H6, s) 7.44 (H2′, H6′, d, J = 1.74) 7.76 (H4′, t, J = 1.77)
180	2,2′,3,4,4′,5,5′-heptabromobiphenyl	7.51 (H6, s) 7.97 (H3′, s) 7.48 (H6′, s)
189	2,3,3′,4,4′,5,5′-heptabromobiphenyl	7.57 (H6, s) 7.58 (H2′, H6′, s)
194	2,2′,3,3′,4,4′,5,5′-octabromobiphenyl	7.49 (H6, H6′, s)
206	2,2′,3,3′,4,4′,5,5′,6-nonabromobiphenyl	7.42 (H6, s)

[a] Adopted from Ballschmitter and Zell, 1980.

The degree of ortho bromine substitution directly influences the UV spectra obtained for PBBs (Dannan, 1982; DeKok et al., 1977). The main band in the UV spectra is caused by a π–π^* electron transition while the k-band is attributed to a charge transfer between the phenyl rings. Because conjugation is energetically favored in a planar biphenyl system, the intensity of the k-band increases with the planarity of the compounds studied. One should expect that increasing ortho halogen substitution would result in a loss in planarity and effect a decrease in the

Table III. Mass Fragmentation Data (Relative Abundance, %) for the Synthetic PBBs (Obtained on a Varian Ch-7a Mass Spectrometer in EI Mode at 70 eV; Samples Introduced by Direct Insertion (Probe Heated at 4 °C/s))

no.[a]	synthetic PBB	M^+	−1 Br	−2 Br
114	2,3,4,4′,5-pentabromobiphenyl	548 (100)		388 (37)
		550 (96)		390 (35)
137	2,2′,3,4,4′,5-hexabromobiphenyl	628 (84)	547 (60)	468 (58)
			549 (58)	
141	2,2′,3,4,5,5′-hexabromobiphenyl	628 (99)	547 (73)	468 (62)
			549 (71)	
156	2,3,3′,4,4′,5-hexabromobiphenyl	628 (100)		468 (37)
159	2,3,3′,4,5,5′-hexabromobiphenyl	628 (100)		468 (37)
180	2,2′,3,4,4′,5,5′-heptabromobiphenyl	706 (100)	627 (62)	546 (50)
		708 (98)		548 (49)
189	2,3,3′,4,4′,5,5′-heptabromobiphenyl	706 (100)		546 (30)
		708 (98)		548 (29)
194	2,2′,3,3′,4,4′,5,5′-octabromobiphenyl	786 (44)	705 (74)	626 (40)
			707 (71)	
206	2,2′,3,3′,4,4′,5,5′,6-nonabromobiphenyl	864 (100)	785 (87)	704 (44)
		866 (98)		706 (45)

[a] Adopted from Ballschmitter and Zell, 1980.

Table IV. GC Properties and Quantitation of the Synthetic PBBs in FireMaster

no.[a]	synthetic PBB	rel ret time[b]	rel resp factor[c]	% compn fireMaster[d] FF-1	% compn fireMaster[d] BP-6
114	2,3,4,4′,5-pentabromobiphenyl	1.122	0.194	nd[f]	0.08
137	2,2′,3,4,4′,5-hexabromobiphenyl	1.777	0.472	nd	nd
141	2,2′,3,4,5′,5-hexabromobiphenyl	1.540	0.338	nd	0.10
153	2,2′,4,4′,5,5′-hexabromobiphenyl[e]	1.432			
156	2,3,3′,4,4′,5-hexabromobiphenyl	1.810	0.100	nd	0.08
159	2,3,3′,4,5,5′-hexabromobiphenyl	1.834	0.088	nd	nd
180	2,2′,3,4,4′,5,5′-heptabromobiphenyl	1.757	0.400	6.00	7.10
189	2,3,3′,4,4′,5,5′-heptabromobiphenyl	1.816	0.252	nd	nd
194	2,2′,3,3′,4,4′,5,5′-octabromobiphenyl	1.794	0.070	nd	nd

[a] Adopted from Ballschmitter and Zell, 1980. [b] Octachloronaphthalene = 1.000. [c] 1 pg of octachloronaphthalene = 1.000. [d] Quantitation was based on GC–MS determinations (ion collection with use of a VG 7070 F double-focusing mass spectrometer of the respective molecular ions in the EI mode). [e] Retention time for congener 153 (major component in fireMaster) presented for comparison purposes. [f] Not detected (detection limit was estimated to be approximately 0.1% of fireMaster, 1000-ng injection).

extinction coefficient of the k-band. Accordingly, our data show that PBBs possessing only one ortho bromine exhibit prominent k-bands in their UV spectra (e.g. 114, 156, 159, and 189) while in the spectra of congeners containing two ortho bromines (137, 141, 180, 194) or three ortho bromines (congener 206) the k-band was not seen (Table I).

Sovocool and Wilson (1982) have reported a so-called ortho-effect in the mass fragmentation of PBBs. The mass spectra of PBBs, which were substituted in the ortho positions, were characteristically different from those that are not. The ratio of the relative frequency $[M - Br]^+$ to $[M - 2\ Br]^+$ was found to be 0.02–0.06 for nonortho- and monoortho-substituted compounds and to be 0.5–1.4 for compounds with two or three ortho bromines. The calculated ratio $[M - Br]^+$ to $[M - 2\ Br]^+$ for the 2,2′-substituted PBBs we synthesized was 1.0–1.93 (Table III). The $[M - Br]^+$ fragment was missing in the spectra from the compounds with only one ortho bromine. As expected, the nonortho-substituted congener 169 did not exhibit this ortho-effect (unpublished data). In a recent publication, Sovocool et al. (1987) showed the enhancement of the $[M - X]^+$ fragment in mass spectra for those molecules substituted in positions 2,2′ and 3,3′ (2,2′ and 5,5′, respectively). The mass spectra of compounds 141, 180, 194, and 206 confirm this observation (Table III).

Retention behavior of each synthetic PBB standard was characterized by capillary GC and is presented in Table IV along with its response factor (relative to octachloronaphthalene). The quantitation of these PBBs in fireMaster BP-6 and fireMaster FF-1 was carried out in the same chromatographic system interfaced with a VG 7070 F double-focusing MS. Quantitation was based on ion collection of the respective molecular ions in the EI mode. This unambiguous method, which takes both retention behavior and molecular weight into account, is independent of response factor differences. The quantitation of congeners 156 and 180 in fireMaster BP-6 is in good agreement with our previous report (Robertson et al., 1984). Differences exist in the quantitation of three minor components of fireMaster FF-1 between our data and those of Orti et al. (1983). Using a quantitation method based on peak areas, they report the presence of congeners 156, 189 (each less than 1% of fireMaster FF-1), and 194 (at 1.65%). We could neither confirm nor reject the presence of these congeners in our sample of fireMaster FF-1, Lot FH 7042. One might expect minor differences in composition in this industrial chemical mixture even within a single batch. Comparison of peak areas however may lead to an overestimation of congener 180, which Orti and coworkers found to be 23.5% of fireMaster FF-1.

ABBREVIATIONS

EI, electron impact; GC, gas chromatography; mp, melting point (not corrected); MS, mass spectrometry; NBS, *N*-bromosuccinimide; PBB, polybrominated biphenyl; PCB, polychlorinated biphenyl; ^1H NMR, proton magnetic resonance; TLC, thin-layer chromatography.

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